

Prediction of the Physical Properties of Very Long-Chain Molecules

R.J. Sadus^{C, S}

Centre for Molecular Simulation, Swinburne University of Technology, Hawthorn, Victoria, Australia

Considerable progress has been achieved in the prediction of the fluid phase properties using equations of state [1]. Unlike other theoretical alternatives, an equation of state can be applied equally to gas, liquid and supercritical states without encountering any conceptual difficulties. Molecular simulation [2] is also being increasingly applied [3] to the physical properties of real fluids but the computational cost for very large molecules means that it is far from a routine tool for predictions. However, in addition to direct prediction, molecular simulation provides valuable data for the validation and improvement of theoretical models. The theoretical backbone of most equations of state is an idealized model for intermolecular repulsion. In the case of simple molecules, this is the concept of a hard-sphere fluid whereas the concept of a hard-sphere chain [1] or hard-convex body chain [4] can be used as the basis of equations of state for real chain-like molecules [5]. Therefore, improvements to the theoretical model provide a direct pathway to improving the prediction of the properties of fluids in general. A direct comparison [6] of theory with simulation data for the compressibility factor and second virial coefficients using theoretical models such as various thermodynamic perturbation theories (TPT1, TPT2, TPT-dimer) indicates that the quality of agreement deteriorates considerably for very large chains. It is important to address this deficiency because it ultimately limits the accuracy of equations of state for real fluids. In this work we make use of recent molecular simulation results to significantly improve the accuracy of a TPT-based equation of state for very long chains. The result is an equation of state that can accurately predict the compressibility factor, and second, third and fourth virial coefficients of hard-sphere chains with up-to 200 (and possibly more) hard-sphere monomers. When this equation is augmented by a suitable attractive term, it can be used to accurately predict the vapor-liquid equilibria of real chain-like molecules, such as the n-alkanes.

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